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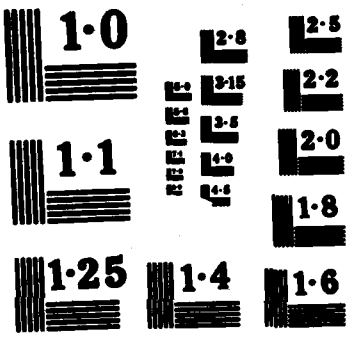

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FOREIGN TECHNOLOGY DIVISION

STUDY OF CROSS-LINKING DENSITY AND THE TYPE OF CROSS LINKAGE IN POLYURETHANE ELASTOMERS

by

L.M. Sergeyeva, Yu. S. Lipatov, N.I. Bin'kevich

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Б б	*Б б*	B, b	С с	*С с*	S, s
В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
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Й й	*Й й*	Y, y	Щ щ	*Щ щ*	Shch, shch
К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

*ye initially, after vowels, and after ъ, ь; e elsewhere.
When written as ё in Russian, transliterate as yё or ё.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	$\sinh^{-1}$
cos	cos	ch	cosh	arc ch	$\cosh^{-1}$
tg	tan	th	tanh	arc th	$\tanh^{-1}$
ctg	cot	cth	coth	arc cth	$\coth^{-1}$
sec	sec	sch	sech	arc sch	sech^{-1}
cosec	csc	csch	csch	arc csch	csch^{-1}

Russian	English
rot	curl
lg	log

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STUDY OF CROSS-LINKING DENSITY AND THE TYPE OF CROSS LINKAGE IN POLYURETHANE ELASTOMERS

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One of the most important problems facing the physical chemistry of polymers is that of synthesizing cross-linked networks with a regular structure, or defect-free networks. This problem is especially important for synthesizing rubbers with increased physicomechanical properties, in particular, high wear resistance. As report [7] suggests, this characteristic is connected with the regularity of the cross-linking structure. From the standpoint of forming a defect-free network, it is obvious that theoretically, such a structure cannot be obtained by the vulcanization of ordinary rubbers because of the statistical nature of the vulcanization process and the presence of different macromolecule conformations in the rubber before vulcanization, as well as their fixation after cross-linking.

The capacity of macromolecules to form different conformations is reflected in the regularity of the cross-linked network obtained from oligomer molecules, as was shown using polyester acrylates as an example [1].

From the standpoint of synthesizing cross-linked polymers with the potentially smallest degree of defectiveness of the network, polyurethane polymers are of special interest. When polyurethane

elastomers are obtained through the macrodiisocyanates that form during the reaction of two moles of polyester and three moles of diisocyanate and cross-linking of the excess of the latter after the chains are lengthened by diamines, it is possible to obtain cross-linked structures in which the cross-linked unit is constructed from identical structural elements [8]. In this case, the same macrodiisocyanate is used both for building the chain, and for cross-linking. Here the dimensions of the cross-linked units can only differ because of the presence of a certain degree of polydispersion in the oligomer polyesters used for the synthesis. In passing, we will note that obviously, the use of oligomers with a narrow molecular-weight distribution will theoretically make it possible to obtain a less defective network.

Obviously, the development of physicochemical methods of evaluating the regularity of the cross-linking structure and their correlation with the cross-linking density are very much needed.

The application of ordinary methods of evaluating the cross-linking density to polyurethanes is complicated by the specific nature of their structure. The capacity of polyurethanes for forming hydrogen bonds leads to the origination of strong cross-linkages determined by intermolecular reactions in them, along with the chemical units. These bonds can be so strong that under certain synthesis conditions, linear polyurethanes can have good high-elasticity and strength properties without additional cross-linking [8].

Cont'd

The purpose of this work is to study the validity of theories that make it possible to evaluate the cross-linking density based on different physical methods for polyurethane elastomers. One of the main parameters that characterize the structure of a cross-linked polymer is the value of the effective cross-linking density or the mean molecular weight of the chain segment between units. The kinetic theory of elasticity and the Flory-Renner theory of swelling [9] are the basis for determining this value. All of these theories were developed for ordinary elastomers, which, in this case, we are considering to be elastomers whose chain consists of units of the same

Cont'd

nature, and which at least do not contain sections with different rigidity.

There are several experimental methods of determining the effective cross-linking density [9, 10]. Some of them were used for determining the cross-linking density in polyurethanes [11].

In our study, we used the methods of evaluating the cross-linking density from data about the equilibrium modulus of high elasticity and about the compression of swollen specimens in order to determine the parameter ψ of the Flory equation, which would also make it possible to make these measurements based on data about swelling.

Table 1. Molar ratios of components during synthesis of elastomers.

(1) Образец	(2) Полиэфир	(3) ТДИ	(4) Сшивающий агент
1	I	1.10	0.035
2	I	1.15	0.070
3	I	1.20	0.100

KEY: (1) Specimen. (2) Polyester. (3) TDTs [toluenediisocyanate]. (4) Cross-linking agent.

Polyurethane elastomers obtained on the basis of the polyester diethylene glycol and adipic acid with a molecular weight of 1600 and toluenediisocyanate were the objects of the study. The cross-linking agent was a mixture of diethanolamine with triethanolamine in a molar ratio of 1:1.5. Three specimens with different ratios of components were studied (Table 1)[1].

The effective cross-linking density was determined based on the kinetic theory of high elasticity which connects the equilibrium modulus with the cross-linking density. The theory's validity for polyurethene was the subject of a special study [14]. The cross-linking density was also determined according to method [10] from data on the compression of swollen specimens. In this case, the following equation was used:

$$\frac{\nu_e}{V} = h_0 S/3A_0 RT, \qquad (1)$$

[1]The authors would like to thank V. G. Sinyavskiy for providing the specimens for the study.

where $\frac{\nu_e}{V}$ - the concentration of cross-linked chains per unit volume, A_0 - the cross-sectional area of the specimen, h_0 - the height of the unswollen undeformed specimen, and S - the slope of the straight line of the dependence of the stress on deformation.

The number of chemical cross-linkages was calculated, on the basis of which the ratio of components taken for synthesis was calculated using the equation:

$$\frac{\nu_e}{V} = \frac{3}{2} C_T, \tag{2}$$

where C_T - the concentration of triethanolamine used for cross-linking [11].

We determined the parameter of the reaction of ψ of the polymer and the solvent based on the kinetic theory of high elasticity and the Flory-Renner theory. According to the kinetic theory,

$$\tau = \frac{\nu_e}{V} RT (\alpha - \alpha^{-2}), \tag{3}$$

where τ - the load, g/cm^2, necessary for obtaining elongation α, $\frac{\nu_e}{V}$ - the effective density of the chains per unit volume. According to the Flory-Renner theory, the value of the effective cross-linking density:

$$\frac{\nu_e}{V} = \frac{-[\ln(1-v_2) + v_2 + \psi v_2^2]}{V_1 \left(v_2^{1/3} - \frac{v_2}{2}\right)}, \tag{4}$$

where v_2 - the volume fraction of the polymer in the swollen network. The value of the parameter ψ is found from equations (3) and (4) with the assumption that the cross-linking density value does not change during swelling. In this case, using methods of determining it based on studying swollen specimens does not make it possible to evaluate the original network; it only gives information about this network in the presence of a solvent, when some of the physical bonds may be broken. Thus, the parameter ψ was calculated from the equation:

$$\psi = \frac{-\ln(1-v_2) - v_2 - \frac{\tau V_1 \left(v_2^{1/3} - \frac{v_2}{2}\right)}{RT(\alpha - \alpha^{-2})}}{v_2^2}. \tag{5}$$

The instrument described in [2] was used to experimentally determine τ and α. The study of swelling was conducted using the procedure described earlier in [3].

Results and Discussion

Table 2 gives the values of the effective cross-linking density $\frac{\nu_e}{V}$ and the values of the mean molecular weights of the segments between the chains M_C calculated by different methods.

Table 2. Values of $\frac{\nu_e}{V}$ and M_C calculated by different methods.

Химический метод (1)		Сжатие набухших образцов (2)		Растяжение ненабухших образцов (3)	
$\frac{\nu_e}{V} \cdot 10^4$	M_c	$\frac{\nu_e}{V} \cdot 10^4$	M_c	$\frac{\nu_e}{V} \cdot 10^4$	M_c
0,35	33 800	0,30	33 000	3,2	3700
0,50	24 000	0,49	25 000	3,4	3300
0,70	20 000	0,51	24 000	4,7	2600

KEY: (1) Chemical method. (2) Compression of swollen specimens. (3) Extension of swollen specimens.

As Table 2 shows, the values of M_C calculated on the basis of the stoichiometric relationships are the largest, and those calculated from the equilibrium modulus - the smallest. The predominance of the values of the effective cross-linking density determined experimentally by physical methods over the cross-linking density found by the chemical method was also observed earlier. This disagreement is caused by the existence of secondary physical bonds determined by the interaction of the chains with each other, besides the chemical cross-linkages [5]. We have already noted that the presence of a large number of hydrogen bonds is characteristic of polyurethanes [13]; these bonds obviously make a large contribution to the value of the effective cross-linking density.

At first glance, the disagreement of the effective cross-linking density determined from the data on the extension of unswollen specimens and the compression of swollen specimens appears surprising. Both of these methods are based on determining the value of the equilibrium high-elasticity modulus, and they ordinarily give us the same results [10]. However, most often this involves a situation when the

physical bonds are formed by wrapping and interlocking of the chains, not intermolecular bonds. In report [14], the differences in the values of the effective cross-linking density determined by different methods is explained by the presence of the solvent, which can break the secondary physical bonds. We can assume that in our case, when conducting tests on the compression of swollen specimens, the solvent weakens the physical bonds, which is the prerequisite for their breaking during deformation.

Table 3. Values of polymer-solvent interaction parameter ψ for the specimens in question.

(1) Растворитель	δ	1			2			3		
		Q	v_2	ψ	Q	v_2	ψ	Q	v_2	ψ
Диоксан (2)	9,8	6,02	0,166	0,16	5,47	0,183	0,12	5,19	0,193	0,14
Нитробензол (3)	10	5,49	0,182	0,17	4,75	0,210	0,16	4,31	0,232	0,22
Циклогексанон (4)	9,3	4,22	0,237	0,35	3,89	0,257	0,31	3,39	0,296	0,38
Метилэтилкетон (5)	9,6	2,87	0,348	0,55	2,77	0,362	0,53	2,61	0,383	0,55
Ацетон (6)	9,8	3,11	0,322	0,55	2,77	0,362	0,55	2,56	0,391	0,58
Бензол (7)	9,2	2,62	0,381	0,59	2,58	0,388	0,56	2,36	0,423	0,60
Ацетонитрил (8)	11,9	3,19	0,313	0,56	3,05	0,328	0,55	2,86	0,349	0,57
Толуол (9)	9,0	1,85	0,514	0,73	1,82	0,548	0,75	1,81	0,553	0,75
о-Ксилол (10)	9,1	1,59	0,630	0,87	1,43	0,67	0,92	1,47	0,682	0,94
CCl_4	8,6	1,46	0,684	0,97	1,46	0,686	0,96	1,45	0,687	0,96
CH_3OH	14,5	1,40	0,715	1,04	1,36	0,731	1,07	1,35	0,742	1,09

NOTE: δ - solubility parameter; 1 - specimen with cross-linking ratio of $3.2 \cdot 10^{-4}$; 2 - $3.4 \cdot 10^{-4}$; 3 - $4.7 \cdot 10^{-4}$ moles/cm^3.

KEY: (1) Solvent. (2) Dioxane. (3) Nitrobenzene. (4) Cyclohexanone. (5) Methylethylketone. (6) Acetone. (7) Benzene. (8) Acetonitrile. (9) Toluene. (10) o-Xylene.

Table 3 gives the values of the interaction parameter ψ determined for the specimens in question, as we indicated earlier. The value of the parameter varies with the change in the thermodynamic quality of the solvent within wide limits. The value $\psi = 0.5$ is the boundary between the solvent and the nonsolvent [15]. As Table 3 shows, toluene is not a solvent for the linear analogs. However, polyurethanes can swell up in it, and as the data on determining the cross-linking density indicate, during the deformation of the swollen specimens, the physical bonds can be broken. This indicates that the physical bonds can also deteriorate in media which are not solvents for linear chains. This phenomenon might be caused by the diphyllic nature of the polyurethane chain, in which sections with different polarity alternate. The solvents used may react differently with different

parts of the polymer chains, acting on different physical bonds.

The values of the parameter ψ can be used to determine the cross-linking density of polyurethanes from data on swelling, but only when this cross-linking agent is used. The use of other cross-linking agents which form long transverse bonds can make its own contribution to the reaction with the solvent, thereby changing the values of the interaction parameter ψ.

Based on the data obtained on the effective cross-linking density determined from the stoichiometric relationships and by physical methods, we can approximately estimate the contribution of particular bonds to the total cross-linking density. The calculations made indicated, as Table 4 shows, that the value of the effective cross-linking density in polyurethanes is primarily determined by the physical secondary bonds which form in the cross-linked network as a result of the interaction of the chains with each other.

Table 4. Structural components of effective cross-linking density.

(1) Образец	(2) Химическая $\frac{\nu_e}{V} \cdot 10^4$	(3) Физическая $\frac{\nu_e}{V} \cdot 10^4$	(4) Общая $\frac{\nu_e}{V} \cdot 10^4$	(5) Химическая, %	(6) Физическая, %
1	0,35	2,85	3,2	11	89
2	0,50	2,90	3,4	15	85
3	0,70	4,00	4,7	16	84

KEY: (1) Specimen. (2) Chemical. (3) Physical. (4) Total.

We know that the cohesion energy density is the criterion for this interaction. We determined the cohesion energy density of the specimens in question, for which we used the method described by Dzhi [6]. Figures 1-3 give the dependences of the swelling ratio Q on the solvent solubility parameter for three of the investigated specimens. According to [6], the maximum of the curves corresponds to the polymer solubility parameter. This gives us a cohesion energy density of the specimens in question equal to 96 cal/cm^3. These values are considerably higher than the corresponding values for ordinary rubbers, which confirms the idea of strong intermolecular interactions in polyurethane elastomers.

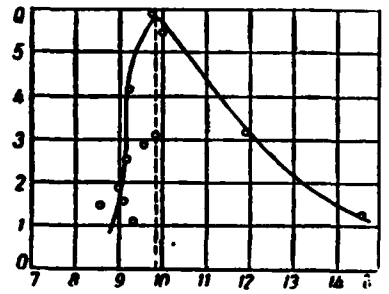

Fig. 1. Dependence of swelling ratio Q on solubility parameter δ of solvent for specimen 1.

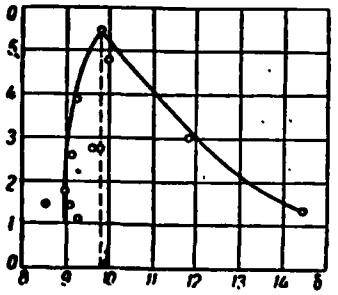

Fig. 2. The same for specimen 2.

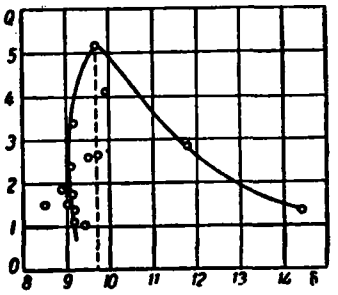

Fig. 3. The same for specimen 3.

Conclusions

1. The swelling of polyurethane elastomers with different cross-linking density was studied in a number of solvents. Using the Flory method, the thermodynamic interaction parameters ψ characterizing the quality of the solvent were determined from the swelling and deformation of the unswollen specimens.

2. The effective cross-linking densities of the elastomers that were studied were determined from the compression of swollen specimens, the value of the equilibrium high-elasticity modulus, and from the stoichiometric relationships. It was shown that the different methods of determining the cross-linking density generate different results.

3. The contribution of the physical bonds to the total cross-linking density was calculated, and it was found that the effective cross-linking density is mainly determined by the physical bonds that form as a result of the reaction of the polar groups of the rubbers.

4. The cohesion energy densities of the polyurethane elastomers were determined, and it was shown that their values exceed the cohesion energy densities of ordinary rubbers because of the presence of strong intermolecular reactions between chains.

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